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(54) MULTILAYER HAVING TITANIUM PEROXIDE-CONTAINING TITANIUM OXIDE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To improve deterioration in association with irradiating with a light or aging and to improve stainproofing, deodorizing, antibacterial properties without impairing a color, gloss or the like of a surface by providing an intermediate film having high affinity to an organic base and exhibiting hydrophilic property after drying between an organic base and a titanium oxide film.

SOLUTION: An intermediate film having high affinity to an organic base and exhibiting hydrophilic property after drying is provided between an organic base and a titanium oxide film. As a material of the organic base, various type thermoplastic resins or thermosetting resins are used. The titanium oxide film is formed by coating a surface of a dried intermediate film with an anatase type titanium oxide dispersion containing a titanium peroxide by a method such as spray coating, flow coating, dip coating, roll coating, spin coating or the like, and curing it. As the intermediate film, a film made of a partially hydrolytic condensate or a film using a titanium peroxide liquid is preferably used, and its film thickness is 0.001 to 1.0 μ m.

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CLAIMS

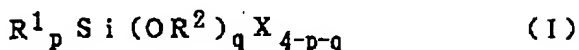
[Claim(s)]

[Claim 1] The multilayer object characterized by having the middle coat with which it is the multilayer object which has an organic base and the titanium oxide film which comes to apply the anatase mold titanium oxide dispersion liquid containing titanium peroxide, and compatibility with the above-mentioned organic base is high between the above-mentioned organic base and the above-mentioned titanium oxide film with a coat, and presents a hydrophilic property after desiccation to it.

[Claim 2] The multilayer object according to claim 1 characterized by forming the titanium oxide film which comes to apply the anatase mold titanium oxide dispersion liquid containing titanium peroxide at low temperature 200 degrees C or less.

[Claim 3] The multilayer object according to claim 1 or 2 characterized by forming a middle coat from one kind or two sorts or more of partial hydrolysis condensates of the alkoxysilane expressed with the following (I) type.

[Formula 1]



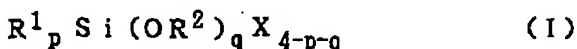
(Among a formula, the alkyl group of carbon numbers 1-5 and X express a halogen atom radical, and, as for p+q, an organic radical univalent in R1 and R2 express the integer of 4-1.)

[Claim 4] The multilayer object according to claim 3 characterized by a middle coat containing colloidal silica.

[Claim 5] The multilayer object according to claim 3 or 4 characterized by containing at least one sort as which a middle coat is chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant.

[Claim 6] Coating liquid for middle coats characterized by containing at least one sort chosen as one sort or two sorts or more of partial hydrolysis condensate lists of alkoxysilane expressed with the following (I) type from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant.

[Formula 2]



(Among a formula, the alkyl group of carbon numbers 1-5 and X express a halogen atom radical, and, as for p+q, an organic radical univalent in R1 and R2 express the integer of 4-1.)

[Claim 7] The multilayer object according to claim 1 or 2 characterized by for a middle coat applying the titanium peroxide solution containing at least one sort chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant, and forming it.

[Claim 8] It is [the description and] a multilayer object according to claim 7 smoothly about a middle

coat being formed at low temperature 200 degrees C or less.

[Claim 9] Coating liquid for middle coats characterized by containing titanium peroxide and at least one sort chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant.

[Claim 10] Lighting covering characterized by consisting of a multilayer object according to claim 1, 2, 3, 4, 5, 7, or 8.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the light catalytic functional material which gave photocatalyst activity to organic base front faces, such as a resin ingredient, resin covering material, or a resin paint ingredient. Furthermore, it is related with the light catalytic functional material using the titanium oxide which has photocatalyst activity, such as decomposition and purification of the organic substance adhering to a base front face, deodorization and purification of the air of the base circumference, or water, and sterilization, by the oxidation reduction reaction which occurs in a detail by optical pumping.

[0002]

[Description of the Prior Art] If the light of the wavelength which has the energy more than the band gap in the titanium oxide which is an optical semi-conductor is irradiated, by optical pumping, an electron will be produced in a conduction band and an electron hole will be produced in a valence band. It is known that the strong reducing power which the electron produced by this optical pumping has, and the strong oxidizing power which an electron hole has will demonstrate functions, such as decomposition and purification of the organic substance adhering to a base material front face, deodorization and purification of the air of the base material circumference or water, and sterilization on the front face of a base material, by that oxidation reduction reaction.

[0003] It is desirable to use in the form fixed on a certain base, when using the function of this titanium oxide practical, and when the quality of the material of that base is a heat-resistant inorganic substance, approaches, such as spreading and baking (JP,60-118236,A) of the sputtering method (JP,60-44053,A) and organic titanate, and blasting, baking of a titania sol (JP,5-253544,A), are adopted. However, when the quality of the material of a base made the organic substance, such as thermoplastics, a subject, heating and baking by high temperature were difficult, and forming the uniform titanium oxide film on a base carried out difficulty, and it had flume *****. Moreover, when titanium oxide was supported directly, the organic substance which is a base being disassembled by the catalysis, or deteriorating is reported (the Otani text, 42 polymer processings, No. 5, p18 (1993)), and there was also a problem that it was necessary to prepare a protective layer between the photocatalyst layers and base front faces which consist of titanium oxide.

[0004] As an approach of solving these problems, the manufacturing method of the photocatalyst object which prepares the first pass which consists of a difficulty resolvability binder on a base in the approach list which pastes up a photocatalyst particle on a base through the difficulty resolvability binder which consists of organic systems, such as inorganic systems, such as water glass and a polysiloxane, or a silicone system polymer, and a fluorine system polymer, and prepares the second layer which consists of a difficulty resolvability binder and a photocatalyst particle on the first pass is indicated by JP,7-171408,A. However, by the approach indicated here, embedding will be carried out and most photocatalyst particles had flaking or the problem that the catalyst function as a photocatalyst was not fully demonstrated in the binder layer.

[0005] On the other hand, although the approach of coating a base with the amorphous mold titanium peroxide of viscosity nature as a binder layer is indicated by JP,10-53437,A as the film production approach that a photocatalyst particle is not buried in a binder layer. Are in the inclination for the thickness of the amorphous mold titanium peroxide layer formed to tend to become thick by this approach, and for the optical physical properties of the titanium oxide that a refractive index is high. It was in the inclination for generating of the interference color and degradation of transparency to take place, and when applying to the base front face accompanied by color or design nature, there was a case of being inconvenient.

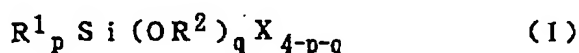
[0006]

[Problem(s) to be Solved by the Invention] This invention aims at offering the light catalytic multifunctional material excellent in antifouling which the exposure of light and degradation by the passage of time are improved sharply, and does not spoil the color of this organic base front face, gloss, etc., deodorization, and antibacterial in organic base front faces, such as a synthetic-resin ingredient, resin covering material, and a resin paint ingredient.

[0007]

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, on an organic base front face, it is oleophilic before desiccation, and its adhesion with an organic base is high, and after desiccation is preparing the middle coat which presents a hydrophilic property and forming the titanium peroxide content titanium oxide film on it, and it came to complete a header and this invention for the above-mentioned technical problem being solvable. Namely, this invention (1) It is the multilayer object which has an organic base and the titanium oxide film which comes to apply the anatase mold titanium oxide dispersion liquid containing titanium peroxide. Between the above-mentioned organic base and the above-mentioned titanium oxide film. The multilayer object characterized by having the middle coat with which compatibility with the above-mentioned organic base is high with a coat, and presents a hydrophilic property after desiccation, (2) The multilayer object given in (1) characterized by forming the titanium oxide film which comes to apply the anatase mold titanium oxide dispersion liquid containing titanium peroxide at low temperature 200 degrees C or less, (3) (1) characterized by forming a middle coat from one kind or two sorts or more of partial hydrolysis condensates of the alkoxysilane expressed with the following (I) type or a multilayer object given in (2), [0008]

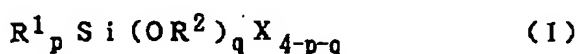
[Formula 3]



[0009] (Among a formula, the alkyl group of carbon numbers 1-5 and X express a halogen atom radical, and, as for p+q, an organic radical univalent in R1 and R2 express the integer of 4-1.)

(4) The multilayer object given in (3) characterized by a middle coat containing colloidal silica, (5) A middle coat A nonionic surfactant, a silicone surfactant, (3) characterized by containing at least one sort chosen from a fluorochemical surfactant and an organic metal surfactant, or a multilayer object given in (4), (6) In one sort or two sorts or more of partial hydrolysis condensate lists of alkoxysilane expressed with the following (I) type, nonionic surfactant, The coating liquid for middle coats, [0010] which are characterized by containing at least one sort chosen from a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant

[Formula 4]



[0011] (Among a formula, the alkyl group of carbon numbers 1-5 and X express a halogen atom radical, and, as for p+q, an organic radical univalent in R1 and R2 express the integer of 4-1.)

A middle coat (7) A nonionic surfactant, a silicone surfactant, (1) characterized by applying the titanium peroxide solution containing at least one sort chosen from a fluorochemical surfactant and an organic metal surface active agent, and being formed, or a multilayer object given in (2), (8) Multilayer object given in (7) characterized by forming a middle coat at low temperature 200 degrees C or less (9) Titanium peroxide, The coating liquid for middle coats characterized by containing at least one sort chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant, (10) it is characterized by consisting of a multilayer object (1), (2), (3), (4), (5), (7), or given in (8) -- it lighting-covers and comes out.

[0012] Hereafter, this invention is explained to a detail. Especially as an ingredient of the organic base used by this invention, although not limited, elastomers, such as urethane rubber, a butyl rubber, and nitril rubber, are mentioned to thermosetting resin, such as thermoplastics, such as the Pori polyethylene, polypropylene, polystyrene, polyacrylic ester, polymethacrylic-acid-ester, polyacrylonitrile, polycarbonate, nylon, polyester, polyvinyl chloride, polyvinylidene chloride, and vinyl fluoride and polyvinylidene fluoride, and epoxy, a melamine, a phenol, polyurethane, and a polyamide, and a pan, for example. Two or more kinds of these resin ingredients can also be used. Moreover, the base with which the coat of the front face was carried out is also contained in the organic base of this invention in the coatings which use these resin as a raw material.

[0013] The titanium oxide film used by this invention can be formed on the dry middle coat front face by applying and stiffening the titanium oxide dispersion liquid (henceforth the coating liquid for titanium peroxide content titanium oxide film formation) of the anatase mold containing titanium peroxide by approaches, such as spray coating, flow coating, DIP coating, roll coating, and spin coating. As this coating liquid for titanium peroxide content titanium oxide film formation, the anatase mold titanium oxide dispersion liquid containing titanium peroxide are used. The anatase mold titanium oxide dispersion liquid containing this titanium peroxide are producible by the approach indicated by JP,10-67516,A. First, a titanium peroxide water solution is prepared. As the method of preparation of this liquid, the approach (JP,9-71418,A) of using a titanium tetrachloride as a start raw material, the approach (JP,62-252302,A) of using titanium hydride as a raw material, the approach (the "building-services and piping work" June, 1998 issue, P.6) of using organic titanate as a raw material, etc. are mentioned. The concentration of a titanium peroxide water solution has 0.001 - 5% of the weight of the desirable range. Productivity is missing in it being less than 0.001 % of the weight, and if it exceeds 5 % of the weight, liquid serves as viscosity, and it will be easy to gel and will be hard coming to treat.

[0014] Next, the dispersion liquid which added the solid-state powder or sol of ultrafine particle anatase mold titanium oxide in the dispersion liquid which carried out thermal denaturation of the titanium peroxide to anatase mold titanium oxide partially, or the above-mentioned titanium peroxide water solution, and were dispersedly obtained [in / for the above-mentioned titanium peroxide water solution / 85-200 degrees C] in it by heat-treatment of 40 - 2 hours under the conditions of liquefied voice are used, using reflux equipment as anatase mold titanium oxide containing titanium peroxide.

[0015] If the anatase mold titanium oxide dispersion liquid containing the titanium peroxide used by this invention mean the dispersion liquid containing a titanium peroxide radical (Ti-O-O-H) component and an anatase mold titanium oxide component and contain both components, they can be adjusted to the component presentation of arbitration in 85-200 degrees C if needed heat-treatment of 40 - 2 hours, or by adjusting the solid-state powder of ultrafine particle anatase mold titanium oxide, or the addition of a sol. The titanium peroxide component of photocatalyst activity is lost at 100%, and an anatase mold titanium oxide component is missing at 100% at film production nature. The content of the titanium peroxide component contained in these dispersion liquid here should just contain the content of an anatase mold titanium oxide component in the X diffraction of the desiccation powder of coating liquid in extent for which the absorption property with a peak of about 410nm can be checked with the light and an ultraviolet radiation part photometer and with which an anatase mold titanium oxide peak is checked that what is necessary is just to carry out extent content.

[0016] 0.001 micrometers or more 1.0 micrometers or less of 0.01 micrometers or more 0.5 micrometers or less of thickness of the titanium oxide film which comes to apply the anatase mold titanium oxide

dispersion liquid containing titanium peroxide are 0.01 micrometers or more 0.3 micrometers or less still more preferably. By making it a thin film, while being able to demonstrate the high transparency of this titanium oxide film, generating of an interference fringe peculiar to the titanium oxide film can also be prevented. Although especially the content of the titanium peroxide contained after film production and in this film is not limited, the peroxidation radical which remained can check the existence by the micro ATR method in infrared spectroscopy as a peak of the peroxidation radical combined with the metal which appears about [900cm⁻¹] in one. However, natural disappearance of the peroxidation radical of a dry paint film can be gradually carried out not after the stable matter but after desiccation, and light and heat can also remove it positively further.

[0017] Formation of the titanium oxide film which comes to apply the anatase mold titanium oxide dispersion liquid containing titanium peroxide is performed by applying and stiffening the liquid which anatase mold titanium oxide distributed in a titanium peroxide solution on the dry middle coat front face by approaches, such as spray coating, flow coating, DIP coating, roll coating, and spin coating. Hardening of this spreading film is advanced by making bridge formation form by heat treatment or ordinary temperature neglect.

[0018] The middle coat in this invention also has the function for making the paint film of the anatase content titanium oxide dispersion liquid containing the titanium peroxide which can be set like a multilayer object formation fault form easily with the function of base protection. As a middle coat for this, compatibility with an organic base is high, and the dry paint film front face after the middle class's spreading is a hydrophilic property, and it is required that adhesion with the titanium peroxide content titanium oxide film should be high. It is getting wet uniformly, without flipping coating liquid for coating liquid to the whole base material surface at the time of spreading as compatibility here is high, and means that adhesion is good for extent in which the desiccation film does not carry out film peeling in the friction test in a cellophane tape (JIS Z 1522 conformity). Moreover, when water is hung down to the interlayer coat front face on which **** dried the hydrophilic property after desiccation, it means not crawling water but getting wet uniformly. That is, when titanium peroxide content anatase mold titanium oxide dispersion liquid are hung down on a middle coat, even after removing the excessive liquid which breadth and a base are made to incline on the whole middle coat uniformly, and flows and falls to it, it is having the compatibility which is extent in which the whole base is uniformly damp.

[0019] In this invention, the film which consists of a partial hydrolysis condensate of an alkoxy run as a middle coat, and the film using a titanium peroxide solution are used preferably. Next, the case where the film which consists of a partial hydrolysis condensate of an alkoxy run as a middle coat is used is explained. If the paint film formed from the partial hydrolysis condensate solution of the alkoxysilane expressed with said formula (I) is good and compatibility with an organic base dries it, this paint film will have a high hydrophilic property, and it will become the high film of water wettability.

[0020] It is required for wettability with an organic base to be good as coating liquid which forms this middle coat, and liquefied alcohols are used as a solvent. If an example is given, a methanol, ethanol, propanol, isopropanol, 1-butanol, 2-butanol, etc. will be mentioned. One sort or two sorts or more can also be mixed and used for this alcohol. the weight of the alkoxysilane which uses the addition of a solvent -- receiving -- the range of the amount of one to 1000 times -- it is the range of the amount of two to 10 times preferably.

[0021] Moreover, a catalyst is added in order to promote hydrolysis condensation. If this catalyst to add promotes hydrolysis, it will not be limited especially and, generally an acid catalyst, a basic catalyst, etc. will be used. As an acid catalyst, organic acids, such as inorganic acids, such as a nitric acid, a sulfuric acid, and a hydrochloric acid, or formic acid, an acetic acid, and a maleic acid, are used. As a basic catalyst, alkaline hydroxides, such as a sodium hydroxide, a potassium hydroxide, and aqueous ammonia, etc. are mentioned. The range of the mole ratio of a catalyst to alkoxysilane is 1/1, and the range of the addition of a catalyst is 1 / 100 - 1/10 preferably. [1000-1]

[0022] As alkoxysilane expressed with the formula (I) used by this invention A tetramethoxy silane, a tetra-ethoxy silane, tetra-propoxysilane, Tetra-butoxysilane, methyl trimetoxysilane, methyl triethoxysilane, A methyl tripropoxy silane, MECHIRUTORI butoxysilane, methyltrichlorosilan,

Methyl tribrom silane, ethyltrimethoxysilane, ethyltriethoxysilane, An ethyl tripropoxy silane, ECHIRUTORI butoxysilane, ethyl trichlorosilan, Ethyl tribrom silane, n-propyltrimethoxysilane, n-propyl triethoxysilane, n-propyl trichlorosilan, n-propyl tribrom silane, n-pro PIRUTORI butoxysilane, n-propyl tripropoxy silane, n-hexyl trimethoxysilane, n-hexyl triethoxysilane, n-hexyl tripropoxy silane, n-hexyl TORIBUTOKI gardenia fruit run, n-hexyl trichlorosilan, n-hexyl tribrom silane, n-decyltrimetoxysilane, n-decyltriethoxysilane, n-DESHIRU tripropoxy silane, n-DESHIRUTORI butoxysilane, n-decyltrichlorsilane, n-decyltribromsilane, phenyltrimethoxysilane, phenyltriethoxysilane, a phenyl tripropoxy silane, a phenyl TORIBUTOKI gardenia fruit run, a phenyl diethoxy KURORU silane, etc. are mentioned. The alkoxysilane whose at least one of 4 substituents combined with Si atom is an alkyl group especially is used preferably.

[0023] In this invention, as for the hydrolysis condensate of alkoxysilane, it is desirable to remain the polar group, especially the hydroxyl group as much as possible as conditions which a middle coat presents a hydrophilic property positively, and the catalyst for this hydrolysis condensation has a desirable acid catalyst. Furthermore, the water solution of inorganic acids, such as a nitric acid, a hydrochloric acid, and a sulfuric acid, is suitable also in an acid catalyst. Since the solution after the catalyst addition which promotes hydrolysis condensation is shifted to hydrophobicity in order that condensation may advance with time and residual hydroxyl groups may decrease in number, it is desirable to use it for a short time, and it is less than 4 hours still more desirably desirably for 1 hour or more for less than 12 hours more than per hour.

[0024] Moreover, in this invention, it is desirable to add colloidal silica in the alcoholic solution of the partial hydrolysis condensate of the above-mentioned alkoxysilane. It makes it possible to be whenever [wide range condensation] and to use the partial hydrolysis condensate of alkoxysilane by adding colloidal silica, and the available time of the solution after acid-catalyst addition also becomes longer than the solution of only alkoxysilane, and it becomes usable [less than 24 hours]. The particle diameter of colloidal silica has 1nm or more desirable 40nm or less, and 5nm or more its 20nm or less is more desirable. Although the process of colloidal silica is not limited, the silica sol made by carrying out the cation exchange of the sodium-silicate solution and the silica sol made by hydrolyzing a silicon alkoxide are used preferably. The addition of colloidal silica can be used to the middle coat weight after desiccation in 0.01 % of the weight - 80% of the weight of the range, and is 10 % of the weight - 50% of the weight of the range preferably.

[0025] Furthermore, in the partial hydrolysis condensate solution of the alkoxysilane of this invention, the thing which is chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant and which add a kind at least is desirable. By containing this surface active agent, the middle coat which consists of the above-mentioned alkoxysilane hydrolysis condensate can raise greatly the coating nature of the coating liquid for titanium peroxide content titanium oxide film formation, and the hydrophilic property of a middle coat, and makes high adhesion and high endurance possible. It is effective in raising the flexibility as a multilayer object of the titanium peroxide content titanium oxide film still more finally formed. The addition of this surfactant is used to the middle coat weight after desiccation in 0.0001 % of the weight - 50% of the weight of the range, and is 0.0001 % of the weight - 10% of the weight of the range preferably.

[0026] If the example which can be used by this invention is given, as a nonionic surfactant A polyethylene-glycol system ester mold ($\text{RCOO}(\text{CH}_2\text{CH}_2\text{O}) \text{ nH}$), An affiliated ether mold ($\text{RO}(\text{CH}_2\text{CH}_2\text{O}) \text{ nH}$), an affiliated alkylphenol mold ($\text{RPhO}(\text{CH}_2\text{CH}_2\text{O}) \text{ nH}$), A polyhydric-alcohol partial ester system sorbitan ester mold and an ester ether system polyoxyethylene sorbitan ester mold as a silicone surfactant What the ethylene glycol chain or the propylene glycol chain combined with the silicone polymer chain with the block polymer mold, the side-chain denaturation mold, or the terminal modification mold as a fluorochemical surfactant Perfluoroalkyl polyoxyethylene ethanol, perfluoroalkyl alkoxylate, and fluorination alkyl ester as an organic metal surfactant [$\text{RO}(\text{CH}_2\text{CH}_2\text{O}) \text{ n}$] $2\text{M}(\text{OC}_4\text{H}_9)_2$ are desirable from excelling in transparency and weatherability. While the silicone surfactant which the ethylene glycol chain or the propylene glycol chain combined with the silicone polymer chain by side-chain denaturation or terminal modification maintains the stability of coating

liquid especially It is desirable especially from it being rich in base material wettability, and weatherability and transparency being further excellent (among a formula, in an alkyl group and Ph, a phenyl group and M express a metal atom and n expresses [R] the integer of 1-100).

[0027] Formation of this middle coat is performed by making an organic base front face apply and harden the partial hydrolysis condensate solution of the alkoxysilane which is coating liquid for middle coats by approaches, such as spray coating, flow coating, DIP coating, roll coating, and spin coating. Hardening of a paint film is advanced by making bridge formation of a coating constituent form by heat treatment or ordinary temperature neglect. To the coating liquid for middle coats, as mentioned above, a kind can be added as being chosen out of colloidal silica and/or a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant as it is few.

[0028] As a middle coat of this invention, the interlayer coat which applies the coating liquid which adds at least one sort chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant, and is obtained, and is formed is also preferably used for a titanium peroxide solution. A titanium peroxide water solution can be prepared by approaches, such as the approach (JP,9-71418,A) of using a titanium tetrachloride as a start raw material, as described above, the approach (JP,62-252302,A) of using titanium hydride as a raw material, and the approach (the "building-services and piping work" June, 1998 issue, P.6) of using organic titanate as a raw material. although it is a water solution, in order that being created by these approaches may speed up desiccation -- polar organic solvents, such as alcohol, -- dilution -- even if it carries out a solvent permutation, it does not interfere (in the case of a water solution, it explains hereafter.).

[0029] If it dries at the temperature of 200 degrees C or less after spreading, since a titanium peroxide water solution will not be transferred to crystalline titanium oxide, it does not have catalytic activity to the extent that an organic base is degraded like anatase mold titanium oxide. In order to carry out thin film homogeneity spreading of the titanium peroxide water solution, a low-concentration titanium peroxide water solution is desirable, and 3 or less % of the weight is desirable by titanium oxide conversion concentration. However, most solution components are water and it was not able to apply the low-concentration titanium peroxide water solution to the base thinly at homogeneity. When the solution which added at least one sort chosen as a titanium peroxide water solution from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant was used as coating liquid for middle coats, this invention persons could apply the titanium peroxide water solution to homogeneity thinly, improved coating nature of the coating liquid for titanium peroxide content titanium oxide film formation, and found out raising the adhesion of the titanium peroxide content titanium oxide film. Moreover, it found out raising the flexibility of this multilayer object on the contrary, without hardly having a bad influence on the weatherability of the multilayer object finally acquired, even if it adds a surfactant. It is desirable from application effectiveness going up [what is 30 or less degrees] from the ability of that whose contact angle over the organic base of a water solution is 40 or less degrees forming a thin uniform coat the 1% of the weight desirable still more preferably in the above-mentioned surfactant, and productivity improving.

[0030] As a nonionic surface active agent, a polyethylene-glycol system ester mold ($\text{RCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), An affiliated ether mold ($\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), an affiliated alkylphenol mold ($\text{RPhO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), A polypropylene-glycol system ester mold ($\text{RCOO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), An affiliated ether mold ($\text{RO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), an affiliated alkylphenol mold ($\text{RPhO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n\text{H}$), A polyhydric-alcohol partial ester system sorbitan ester mold and an ester ether system polyoxyethylene sorbitan ester mold as a silicone surfactant What the ethylene glycol chain or the propylene glycol chain combined with the silicone polymer chain with the block polymer mold, the side-chain denaturation mold, or the terminal modification mold as a fluorochemical surfactant Perfluoroalkyl polyoxyethylene ethanol, perfluoroalkyl alkoxylate, and fluorination alkyl ester as an organic metal surfactant [$\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n$] $2\text{M}(\text{OC}_4\text{H}_9)_2$ are desirable from excelling in transparency and weatherability. While the silicone surfactant which the ethylene glycol chain or the propylene glycol chain combined with the silicone polymer chain by the block polymer mold, side-chain denaturation, or terminal modification maintains the stability of coating liquid especially It is desirable especially from it being rich in base material

wettability, and weatherability and transparency being further excellent (among a formula, in an alkyl group and Ph, a phenyl group and M express a metal atom and n expresses [R] the integer of 1-100). [0031] Moreover, although the addition of this surface active agent is satisfactory if it is an amount below the amount of solid content of a titanium peroxide water solution (titanium oxide conversion), it is usually added in 1 - 1/100 to the amount of solid content of a titanium peroxide solution. Formation of a middle coat is based on making a titanium peroxide water solution apply and harden the coating liquid which adds at least one sort chosen from a nonionic surfactant, a silicone surfactant, a fluorochemical surfactant, and an organic metal surfactant, and is obtained on an organic base front face by approaches, such as spray coating, flow coating, DIP coating, roll coating, and spin coating. Hardening of a paint film is advanced by making bridge formation of a coating constituent form by heat treatment or ordinary temperature neglect.

[0032] When heat-treating to an organic base, it is desirable to heat in 10-degree-C or more temperature requirement 200 degrees C or less, and 30 more degrees-C or more temperature requirement 150 degrees C or less is desirable. This middle coat of heat-treating at the temperature exceeding 200 degrees C, when an organic base will receive heat deformation and heat deterioration and it will use a titanium peroxide solution as a middle coat, if it heats at the temperature exceeding 200 degrees C is not desirable from carrying out phase transition to an anatase mold from an amorphous mold.

[0033] It is desirable that it is the 0.001-micrometer or more range of 1.0 micrometers or less in respect of base material protection nature and transparency, more preferably, a crack with very small after film production it 0.05-micrometer or more being 0.5 micrometers or less etc. stops being able to enter easily, and, as for the thickness of the middle coat by which paint film formation is carried out on an organic base front face, it is desirable that it is [0.1 more micrometer or more] 0.4 micrometers or less in respect of productivity and thickness control. It becomes possible to give photocatalyst functions, such as antifouling, deodorization, and sterilization, to a product, without spoiling the design nature which the conventional product has, if lighting covering, a molding signboard, lighting fitting, OA equipment, various accessories, or an outer wall by which resin paint was carried out made of resin etc. applies the paint film in this invention to lighting covering and lighting fitting especially using an arc tube. Moreover, when the spreading film of a titanium peroxide solution is used for a middle coat, since the antistatic engine performance which titanium peroxide has can be given, it makes it possible to increase the antifouling property of a product further.

[0034]

[Embodiment of the Invention] Hereafter, an example and the example of a comparison explain this invention to a detail further. As an organic base, the acrylic resin plate

"DERAGURASUA" (10RA10cm) by Asahi Chemical Industry Co., Ltd. was used. Pretreatment (surface cleaning) was immersed for about 1 minute into isopropyl alcohol (Wako Pure Chem best) in the base, and degreased the front face.

[0035]

[The example 1 of manufacture] If about 100ml of aqueous ammonia is added to 10ml of 60 % of the weight (TiCl₄) water solutions of <manufacture of titanium peroxide water solution> titanium tetrachlorides 2.5% of the weight and they are neutralized to pH 6-7, the precipitate of the hydroxylation titanium (Ti₄ (OH)) of light blueness white will be produced. When 1.8l. of ion exchange water is added to 40g of wet solid content, it considers as a slurry after washing and 0.2l. of hydrogen peroxide solution was made to act 30% by repeating a decantation for this sediment, the titanium peroxide water solution of yellow transparence was obtained. Concentration adjustment of this was carried out so that it might become 1.7% of the weight (titanium oxide conversion) using an evaporator.

[0036]

[The example 2 of manufacture] When heat-treatment was carried out for the titanium peroxide water solution obtained in the example 1 of <manufacture of titanium peroxide content anatase mold titanium oxide dispersion liquid> manufacture at 100 degrees C for 6 hours, the titanium peroxide content anatase mold titanium oxide dispersion liquid which the great portion of titanium peroxide transferred to the particle of the crystalline titanium oxide of an anatase mold were obtained. When the number

average particle diameter of the crystal particle distributed in this liquid was measured with the particle-size-distribution plan by optical dispersion, it was 10nm. This solution was condensed using the evaporator and it adjusted to 2.4% of the weight.

[0037]

[Example 1] 1.8g of 0.01-N hydrochloric acids was added in the solution which added ethanol 46g to methyl trimetoxysilane 13.6g, and what was stirred for 1 hour was used as the coating liquid for middle coats. The spray coat of the spray gun (Anest Iwata RG 2-2) was used and carried out to the acrylic resin base (1.5mm in thickness) of 10cm angle which degreased this coating liquid, and it dried on 60 degrees C and the conditions for 10 minutes, and could be the 1st layer. Subsequently, the multilayer object which similarly carries out the spray coat of the titanium peroxide content anatase mold titanium oxide dispersion liquid obtained in the example 2 of manufacture, dries for 30 minutes and is made into the 2nd layer 80 degrees C was acquired. Thickness was 0.4 micrometers when SEM observation of the cross section of the base which carried out the paint film was carried out. Moreover, the analysis of Ti concentration distribution to the titanium peroxide content anatase mold titanium oxide layer was 0.1 micrometers. Furthermore, it checked that detected [about / 900cm - / one] the peak of the titanium peroxide origin, and the peroxidation radical existed by the micro infrared spectroscopy on the front face of a paint film (Bio-Rad make FTS-169).

[0038]

[Example 2] After mixing ethyltriethoxysilane 7.5g and ethyl silicate (average-degree-of-polymerization tetramer by COL coat company) 7.5g, added 24g of nitric-acid water solutions 2% after dilution, it was made to stir and hydrolyze by ethanol 112g, and the undiluted solution was obtained. Then, the undiluted solution was diluted with isopropanol 5 times, and the coating liquid for middle coats was obtained. The DIP coat was carried out to the acrylic resin base (1.5mm in thickness) of 10cm angle which degreased the coating liquid for these middle coats, and the 1st layer was formed by 60 degrees C and desiccation for 10 minutes. Subsequently, the multilayer object which carries out the DIP coat of the titanium peroxide content anatase mold titanium oxide dispersion liquid obtained in the example 2 of manufacture, dries in 80 degrees C and 30 minutes, and is made into the 2nd layer was acquired. Thickness was 0.4 micrometers when SEM observation of the cross section of the base which carried out the paint film was carried out. Moreover, the analysis of Ti concentration distribution to the titanium peroxide content anatase mold titanium oxide layer was 0.1 micrometers. Furthermore, it checked that detected [about / 900cm - / one] the peak of the titanium peroxide origin, and the peroxidation radical existed by the micro infrared spectroscopy on the front face of a paint film.

[0039]

[Example 3] After mixing tetra-ethoxy silane 3.5g and ethyl ethoxy silane 3.5g, diluted with ethanol 112g, and added 24g of hydrochloric-acid water solutions 2%, it was made to stir and hydrolyze, and the undiluted solution was obtained. Then, the undiluted solution was diluted with isopropanol 5 times, and the coating liquid for middle coats was obtained. The spin coater (Mikasa, Inc 1 H-D2) was used for the acrylic resin base (1.5mm in thickness) of 10cm angle which degreased the coating liquid for these middle coats, the spin coat was carried out by 2000rpm, and the 1st layer of 0.2 micrometers of thickness was formed by 60 degrees C and desiccation for 10 minutes. Subsequently, the multilayer object which carried out the spin coat of the titanium peroxide content anatase mold titanium oxide dispersion liquid obtained in the example 2 of manufacture by 500rpm, dried in 80 degrees C and 30 minutes, and was made into the 2nd layer of 0.5 micrometers of thickness was acquired.

[0040]

[Example 4] The DIP coat of the coating liquid which added methanol silica sol (Nissan Chemical Industries, Ltd. make) 2g was carried out to the acrylic resin base (1.5mm in thickness) of degreased 10cm angle, and the 1st layer of 0.3 micrometers of thickness was formed in the coating liquid for middle coats of an example 1, and 18g of solutions produced similarly by 60 degrees C and desiccation for 10 minutes. Subsequently, the multilayer object which carries out the DIP coat of the titanium peroxide content anatase mold titanium oxide dispersion liquid obtained in the example 2 of manufacture, dries in 80 degrees C and 30 minutes, and is made into the 2nd layer of 0.5 micrometers of

thickness was acquired.

[0041]

[Example 5] 2g ([by Kao Corp.] clean through 710 M) of nonionic surfactants of a polyethylene-glycol system alkyl ether mold was added in the coating liquid for middle coats of an example 1, and 18g of solutions produced similarly, and coating liquid was prepared. The spin coat was carried out to the acrylic resin base (1.5mm in thickness) of 10cm angle which degreased this coating liquid by rotational frequency 1500rpm, and the 1st layer of 0.05 micrometers of thickness was formed by 60 degrees C and desiccation for 10 minutes. Subsequently, the spin coat of the anatase mold titanium oxide dispersion liquid created in the example 2 of manufacture was carried out by rotational frequency 300rpm, and 80 degrees C and the multilayer object for 30 minutes which is dried and is made into the 2nd layer of 0.6 micrometers of thickness were acquired.

[0042]

[Example 6] The coating liquid which added 5g (Nippon Oil & Fats Co., Ltd. make NS-210) of nonionic surfactants of 8% of the weight of a polyethylene-glycol system alkylphenyl ether mold in 95g of titanium peroxide water solutions produced in the example 1 of manufacture was prepared. It was 20 degrees when the contact angle over the acrylic resin base material of this coating liquid was measured with the contact angle plan (CA-S150 mold made from Consonance Interface Science). The spin coat was carried out to the acrylic resin base (1.5mm in thickness) of 10cm angle which degreased this coating liquid by rotational frequency 500rpm, and the 1st layer of 0.1 micrometers of thickness was formed by 60 degrees C and desiccation for 10 minutes. Subsequently, after diluting with distilled water the titanium peroxide content anatase mold titanium oxide dispersion liquid created in the example 2 of manufacture so that it may become 1.2% of the weight, the rotational frequency 500rpm spin coat was carried out, and 80 degrees C and the multilayer object for 30 minutes which is dried and is made into the 2nd layer of 0.1 micrometers of thickness were acquired.

[0043]

[Example 7] The coating liquid which added 5g of nonionic surfactant (Nippon Oil & Fats Co., Ltd. make NS-210) water solutions of 8% of the weight of a polyethylene-glycol system alkylphenol mold in 95g of titanium peroxide water solutions produced in the example 1 of manufacture was prepared. The spin coat was carried out to the acrylic resin base (1.5mm in thickness) of 10cm angle which does not pretreat cleaning of this coating liquid by rotational frequency 1500rpm, and the 1st layer of 0.05 micrometers of thickness was formed by 60 degrees C and desiccation for 10 minutes. Subsequently, the spin coat of the anatase mold titanium oxide dispersion liquid which make the titanium peroxide solution created in the example 2 of manufacture a film production agent was carried out by rotational frequency 300rpm, and 80 degrees C and the multilayer object for 30 minutes which is dried and is made into the 2nd layer of 0.2 micrometers of thickness were acquired.

[0044]

[Example 8] The coating liquid which added 5g of silicone system surfactant FZ2105 (Nippon Unicar make) water solutions of 8% of the weight of a side-chain denaturation mold was adjusted to 90g of titanium peroxide water solutions produced in the example 1 of manufacture. The titanium peroxide water solution which carried out [above-mentioned] adjustment with the rotational speed of 1500rpm was coated with the spin coater (Mikasa, Inc 1 H-D2), using the Asahi Chemical Industry acrylic board "DERAGURASUA" (2mm in 10cm angle, thickness) as a base, stoving was carried out in oven for 60 degrees C and 15 minutes, and the 1st layer membrane of 0.05 micrometers of thickness was formed. Here, the contact angle of the solution to the base before coating was 15 degrees. Subsequently, the titanium peroxide content anatase mold titanium oxide dispersion liquid produced in the example 2 of manufacture were applied with the rotational speed of 1500rpm by the above-mentioned spin coater, 80 degrees C and stoving for 30 minutes were performed, and the multilayer object which makes 0.05 micrometers of thickness the 2nd layer was acquired.

[0045]

[Example 9] 5g of isopropanol liquid of the silicone system surfactant (Nippon Unicar make L77) of 0.8% of the weight of a side-chain denaturation mold was added in 90g of titanium peroxide water

solutions produced in the example 1 of manufacture, and coating liquid was adjusted to them. Using an acrylic board (DERAGURASUA by Asahi Chemical Industry Co., Ltd. (2mm in 10cm angle, thickness)) as a base, in the spin coater (Mikasa, Inc 1 H-D2), with the rotational speed of 500rpm, the titanium peroxide water solution which carried out [above-mentioned] adjustment was coated, oven performed stoving for 60 degrees C and 15 minutes, and the 1st layer membrane of 0.1 micrometers of thickness was formed. Here, the contact angle of the solution to the base before coating was 3 times.

[0046] Subsequently, the titanium peroxide content anatase mold titanium oxide dispersion liquid produced in the example 2 of manufacture were applied with the rotational speed of 300rpm by the above-mentioned spin coater, 80 degrees C and stoving for 30 minutes were performed, and the multilayer object which makes 0.2 micrometers of thickness the 2nd layer was acquired. The engineering-plastics object which supported the photocatalyst on the front face was acquired. Thickness was 0.3 micrometers as a result of observing the cross section of the coating film of this sample with a scanning electron microscope (SEM).

[0047]

[Example 10] 0.4g (product made from Sumitomo 3M FC-430) of 50 % of the weight solutions of butyl carbitols which are a fluorine system nonionic surface active agent was added in 90g of titanium peroxide water solutions produced in the example 1 of manufacture, and coating liquid was adjusted to them. As a base, the titanium peroxide water solution which carried out [above-mentioned] adjustment with the rotational speed of 1000rpm was coated with the spin coater (Mikasa, Inc 1 H-D2) using the polycarbonate resin plate (SHINKOLITE by Mitsubishi Rayon Co., Ltd.) of degreased 10cm angle, for 60 degrees C and 15 minutes, oven performed stoving and the 1st layer membrane of 0.05 micrometers of thickness was formed. Here, the contact angle of the solution to the base material before coating was 28 degrees. Subsequently, the titanium peroxide water solution which was produced in the example 2 of manufacture and which carried out anatase crystal denaturation was applied with the rotational speed of 1000rpm by the above-mentioned spin coater, 80 degrees C and stoving for 30 minutes were performed, and the multilayer object which makes 0.15 micrometers of thickness the 2nd layer was acquired.

[0048]

[The example 1 of a comparison] In 20g of 5g [l.] water solutions of silane coupling agent N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane (Shin-Etsu Chemical Co., Ltd. make) The liquid which added and prepared colloidal silica (Snow tex XS by Nissan Chemical Industries, Ltd.) 2g The rotational frequency 5000rpm spin coat was carried out to the degreased acrylic resin base (1.5mm in thickness) in the spin coater (Mikasa, Inc 1 H-D2), 60 degrees C and desiccation for 10 minutes were performed, and the 1st layer of 0.2 micrometers of thickness was formed. Next, the spin coat of the titanium peroxide content anatase mold titanium oxide dispersion liquid created in the example 2 of manufacture was carried out by 500rpm, and 80 degrees C and the multilayer object for 30 minutes which is dried and is made into the 2nd layer of 0.2micro of thickness were acquired. In examples 3-10 and the example 1 of a comparison, thickness measurement was converted into thickness from the reinforcement of Si and Ti in fluorescence-X-rays measurement. The conversion factor was computed based on the observation thickness in the SEM observation obtained in the example 1.

[0049] The adhesion of the paint film of the adhesion multilayer object test piece of the <evaluation 1 of the paint film engine performance> and a paint film is JIS to the paint film front face of a sample. Z The cellophane tape specified to 1522 was stuck, this was torn off further, and the existence of paint film exfoliation was investigated.

[Valuation basis]

A: completely -- exfoliation-less B: -- partial -- Cwith exfoliation: -- total light transmission with a wavelength of 550nm was measured for each test piece using the light and an ultraviolet radiation spectrophotometer (Jasco Corp. make V-550) by making into a reference the acrylic resin base or polycarbonate resin base which performed only transparency cleaning processing of exfoliation and a paint film completely.

- The accelerated weathering test by the xenon arc type was performed on condition that the rainfall for test time 1000 hours using the sunshine WEZAO meter Ciby atlas company35 mold to the weatherproof

test piece of a paint film for the black panel temperature of 63 degrees C, a 120-minute cycle, and 18 minutes. The same valuation basis as the adhesion test of (1) estimated the sample after a trial.

- The acrylic resin base which supported the titanium peroxide content titanium oxide of a light catalytic magnitude the angle of 10cm was installed in the 3l. TEDORA bag. Into this container, the mixed gas of air and an acetaldehyde was added so that acetaldehyde concentration might be set to 100 ppm. It is ultraviolet-rays on-the-strength 2 mW/cm² to a support sample. The acetaldehyde gas concentration after a 2-hour exposure and inside a container was measured for the light of the black light (Matsushita Electric make) by the gas chromatograph, and the decrement estimated photocatalyst activity.

[Valuation basis]

A:5 ppm or less of evaluation results of the above-mentioned examples 1-10 and the example 1 of a comparison are shown in the B:5 - 50ppm C:50 ppm or more following table 1.

[0050]

[Table 1]

	初期密着性	耐候性	光触媒性	光線透過率
実施例1	A	A	A	95%
実施例2	A	A	A	95%
実施例3	A	A	A	95%
実施例4	A	A	A	95%
実施例5	A	A	A	90%
実施例6	A	A	A	92%
実施例7	A	A~B	A	95%
実施例8	A	A	A	95%
実施例9	A	A	A	95%
実施例10	A	A~B	A	90%
比較例1	A	C	B	80%

[0051] The test piece after surface resistivity film production desiccation of the <performance evaluation 2 of a paint film> and a paint film was kept under **** of 23 degrees C and 50%RH for 24 hours, and it measured using the Toa Electronics surface-electrical-resistance measuring instrument (SME-8310).

- the tar of a paint film -- using resolvability color color difference meter CR-200b (Minolta make), the yellow index on the front face of a sample (YI) was measured first, and it was referred to as YI0. next, from a tip, a photocatalyst side is turned down, the test piece is set to the top face of a cylinder with a diameter [of 6.7cm], and a height of 20cm, one mild seven are burned 1.5cm from the lower part, and it is filled with the smoke of tobacco in a cylinder -- making -- a sample catalyst side -- tar -- dirt is made to adhere The yellow index at this time was set to YI1. Next, the high-pressure mercury-vapor lamp of 400W was irradiated on the sample front face, and the yellow index YI2 of 48 hours after was measured. tar -- the degree type defined resolvability.

[0052] (Tar resolvability) = {1-(YI2-YI0)/(YI1-YI0)} x100 (%)

- After irradiating a sample front face by ultraviolet-rays on-the-strength 1 mW/m² for 2 hours using the black light blue fluorescent lamp of hydrophilic 20W of a paint film, the water contact angle of a photocatalyst side was measured using the contact angle meter CA-S150 mold (product made from Consonance Interface Science). The evaluation result of examples 3, 6, 8-10 is shown in the following table 2.

[0053]

[Table 2]

	第1層コーティング液中の界面活性剤の種類	第2層コーティング液中のアナターゼ変性過酸化チタン溶液濃	表面抵抗率 (Ω/\square)	ヤニ分解性	水接触角 ($^{\circ}$)
実施例3	—	2.4	2.60E+14	88%	0
実施例6	NS210	1.2	2.64E+09	84%	0
実施例8	FZ2105	2.4	1.29E+10	85%	0
実施例9	L77	2.4	3.35E+09	90%	0
実施例10	FC-430	2.4	1.59E+10	83%	0

(注)有機基体として用いたアクリル樹脂「デラグラスA」およびポリカーボネート樹脂「SHINKOLITE」の表面抵抗率は、両者とも無限大であった。

[0054]

[Effect of the Invention] The photocatalyst multilayer object of this invention has high adhesion with a base, and it excels in weatherability, and by improvement in the coating nature by homogeneity thin film spreading, transparency is high, the photocatalyst object which does not spoil base design nature, such as a color and gloss, is realized, and the outstanding photocatalyst activity, such as antifouling, deodorization, and antibacterial, is discovered under sunlight and the indoor illumination light. Moreover, the photocatalyst multilayer object using the coat which comes to apply the titanium peroxide solution containing a surface active agent to a middle coat has the effectiveness of excelling in antifouling property especially from the thing for which it has antistatic ability.

[Translation done.]